

ELECTROCHEMISTRY OF MESOPONE-MYOGLOBIN: A
FUNCTIONAL MODEL OF THE HEME CD1 NITRITE
REDUCTASES

Patrick Farmer, Michael Cohen, Chad Immoos, Kae
Chang

Department of Chemistry
University of California, Irvine
Irvine CA 92697-2025

Heme cd₁ nitrite reductases, which catalyze the conversion of nitrite to NO, contain an unusual Fe-dioxoisobacteriochlorin active site cofactor. A functional protein-based model was formed by reconstitution of Fe^{III}(4-mesoporphyrinone) into apomyoglobin to afford mesopone myoglobin, MpMb. Electrochemical reactivity was analyzed using MpMb cast in thin surfactant films on graphite electrodes. The Fe^{III}/ Fe^{II} couple of MpMb/ddab is shifted ca. + 60 mV relative to native Mb/ddab. In the presence of nitrite, sequential voltammograms show a loss of the Fe^{III/II} couple, indicative of a bulk reaction of nitrite with the Fe^{II} state of MpMb. Solution-based studies confirm that the Fe^{II} state reacts with nitrite to form a stable NO-Fe^{III}, as seen in the heme cd₁ enzymes. Additionally, voltammetry of MpMb under nitrite or nitric oxide generates a reversible couple attributed to reduction of Fe^{II}(NO) to the Fe^{II}(NO⁻), or nitroxyl state. The potential of this reduction is over 150 mV more positive than that in native NO-Mb. The enhanced stability of this species inhibits further catalytic reduction of nitrite and nitric oxide by MpMb.